



Evaluating the Collection Efficiency of Carbonyl Compounds Using TO-11A

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Outline

1. Why carbonyl compounds?
2. Sampling and analysis method for ambient air
3. Collection Efficiency Studies
4. Future Plans
5. Conclusions



Why Carbonyl Compounds?

- Carbonyl compounds: highly reactive, possibly carcinogenic substances.
- Sources of carbonyls
 1. Combustion (motor vehicles, power plants)
 2. Industrial processes (rubber, tanning, food)
 3. Indoor sources (furniture, insulation, tobacco smoke)
 4. Atmosphere

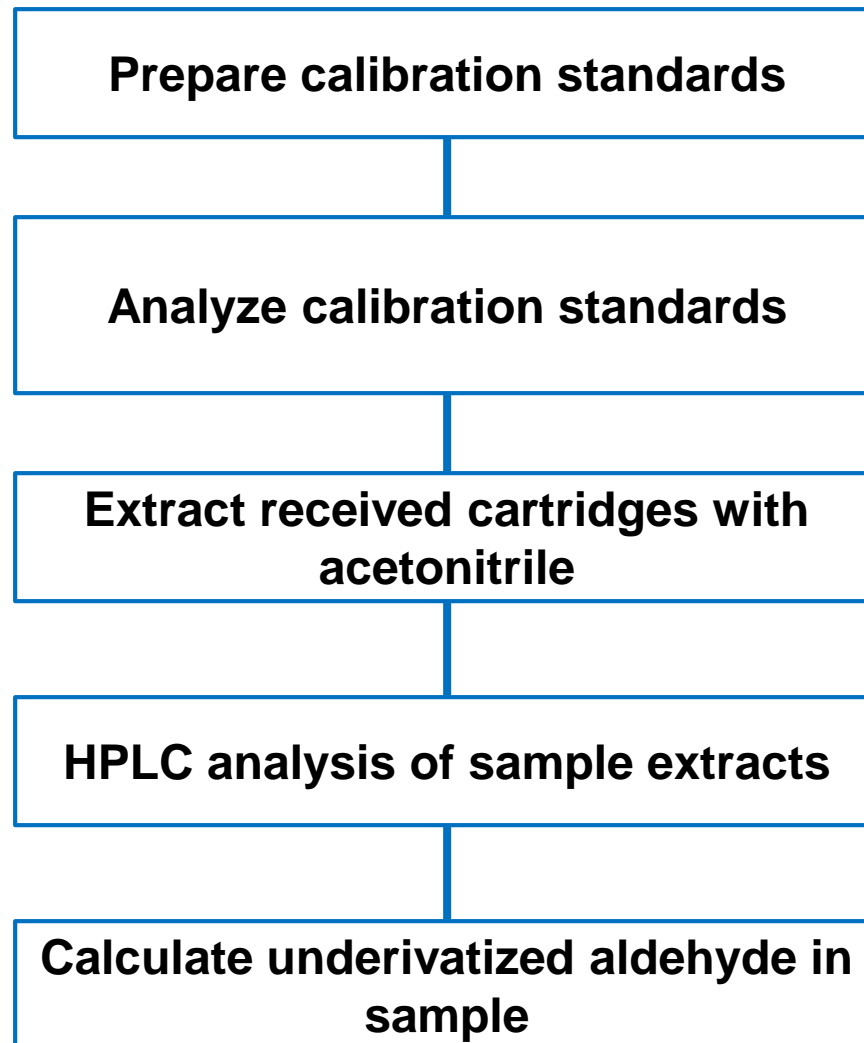


Carbonyl Sampling and Analysis

- Sampling for carbonyl compounds since 1983 using EPA Compendium Method TO-11A
- Collection on DNPH-coated cartridges using ERG sampling system with denuder-style ozone scrubber
- Cartridges extracted with acetonitrile and analyzed on HPLC



Carbonyl Sampling and Analysis





Why Collection Efficiency Studies?



Concerns with TO-11A Method

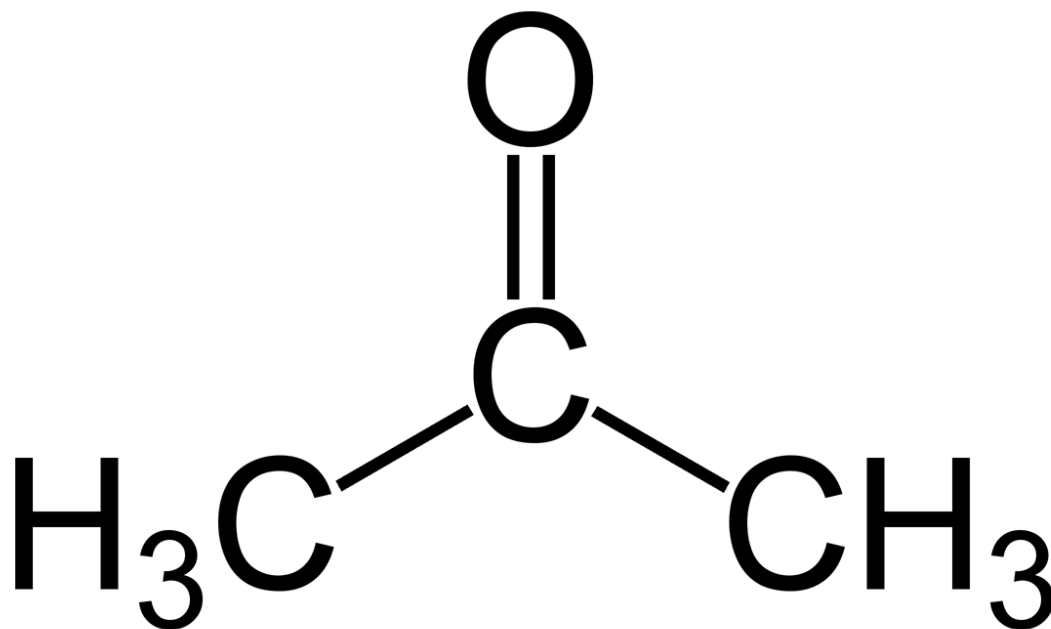
Formaldehyde

Acetaldehyde



Concerns with TO-11A Method

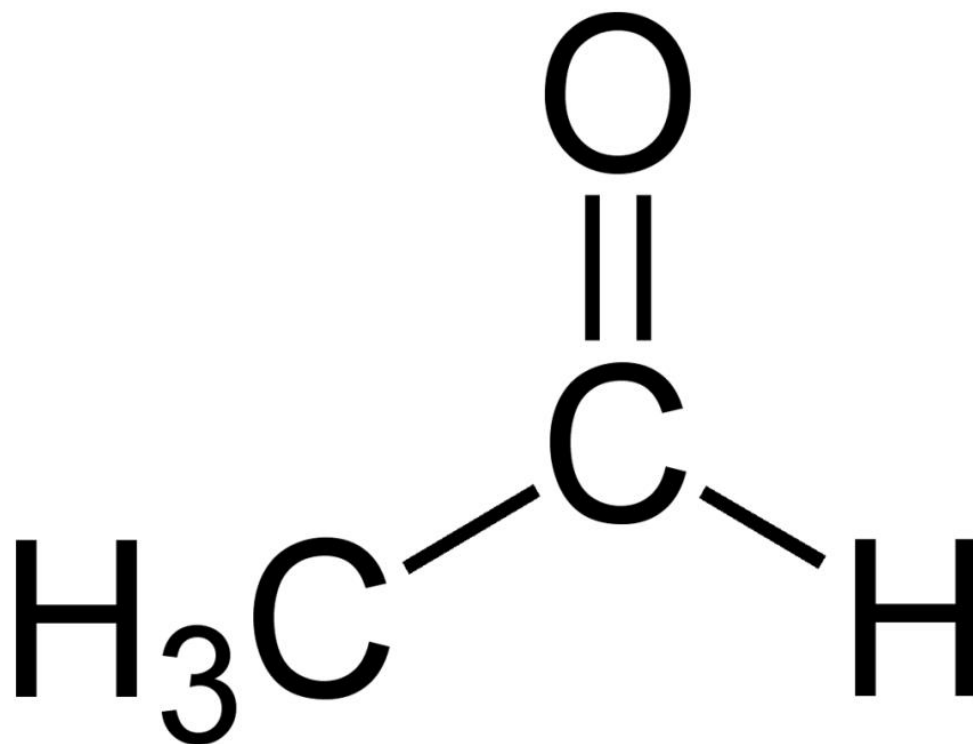
Formaldehyde: Values for this compound may be artificially high because of 2,4-dinitrophenylazide formation





Concerns with TO-11A Method

Acetaldehyde: Values for this compound may be low due to high humidity





Collection Efficiency Study: Procedures

- Ambient air sampling performed at ERG office in Morrisville, NC
- One spiked and one unspiked Waters DNPH sampling tube
- Spike level: 0.6 nanograms of analyte per sample tube = 0.48 ppbv formaldehyde, 0.33 ppbv acetaldehyde.



Collection Efficiency Study: Procedures





Collection Efficiency Study: Procedures

- Sample time and spike time remains the same for each study day
- One spiked tube placed in sample refrigerator as QC check for each day
- Seven sampling days at full flow (700-800 cc/min), three sampling days at half flow (400-500 cc/min)

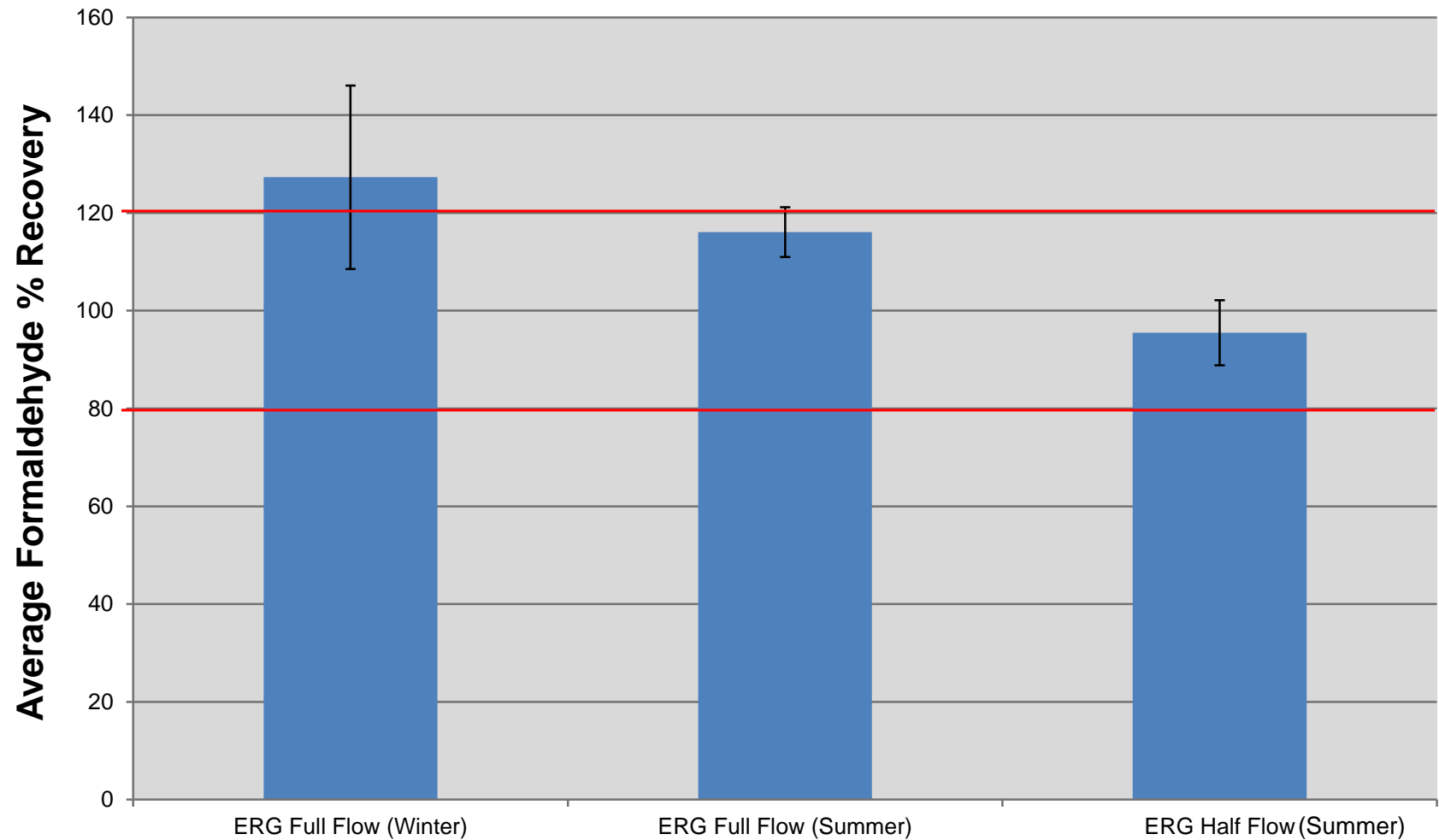


Collection Efficiency Study: Procedures

$$\% \text{ Recovery} = \frac{\text{Spiked Sample} - \text{Unspiked Sample}}{\text{Spiked QC}}$$



Study Results: Formaldehyde





Study Results: Formaldehyde

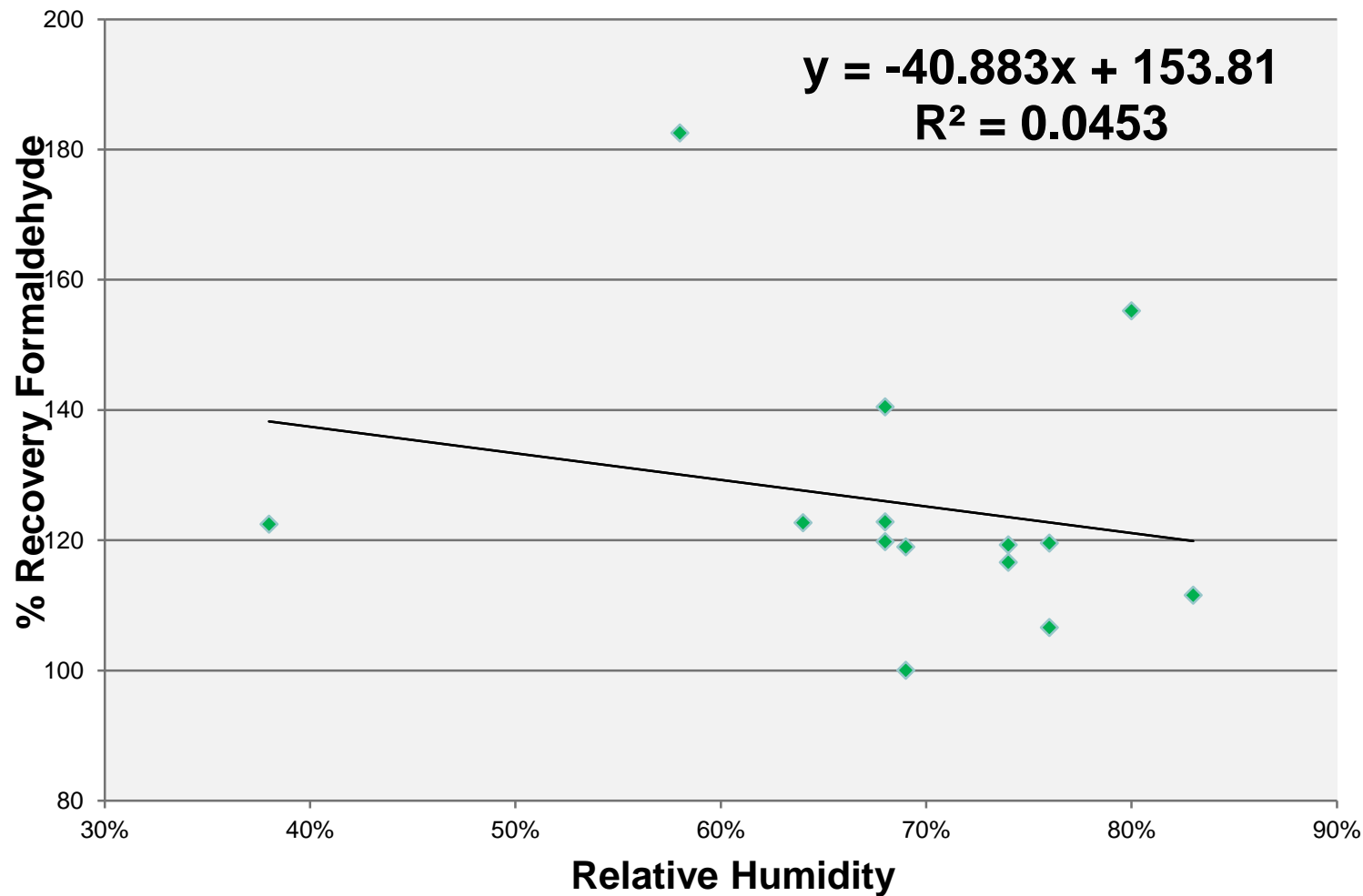
Average % Recovery

ERG Full Flow (Winter) <i>7 samples</i>	127.30% (\pm 18.77%)
ERG Full Flow (Summer) <i>7 samples</i>	116.07% (\pm 5.09%)
ERG Half Flow (Summer) <i>3 samples</i>	95.49% (\pm 6.64%)



Study Results: Formaldehyde

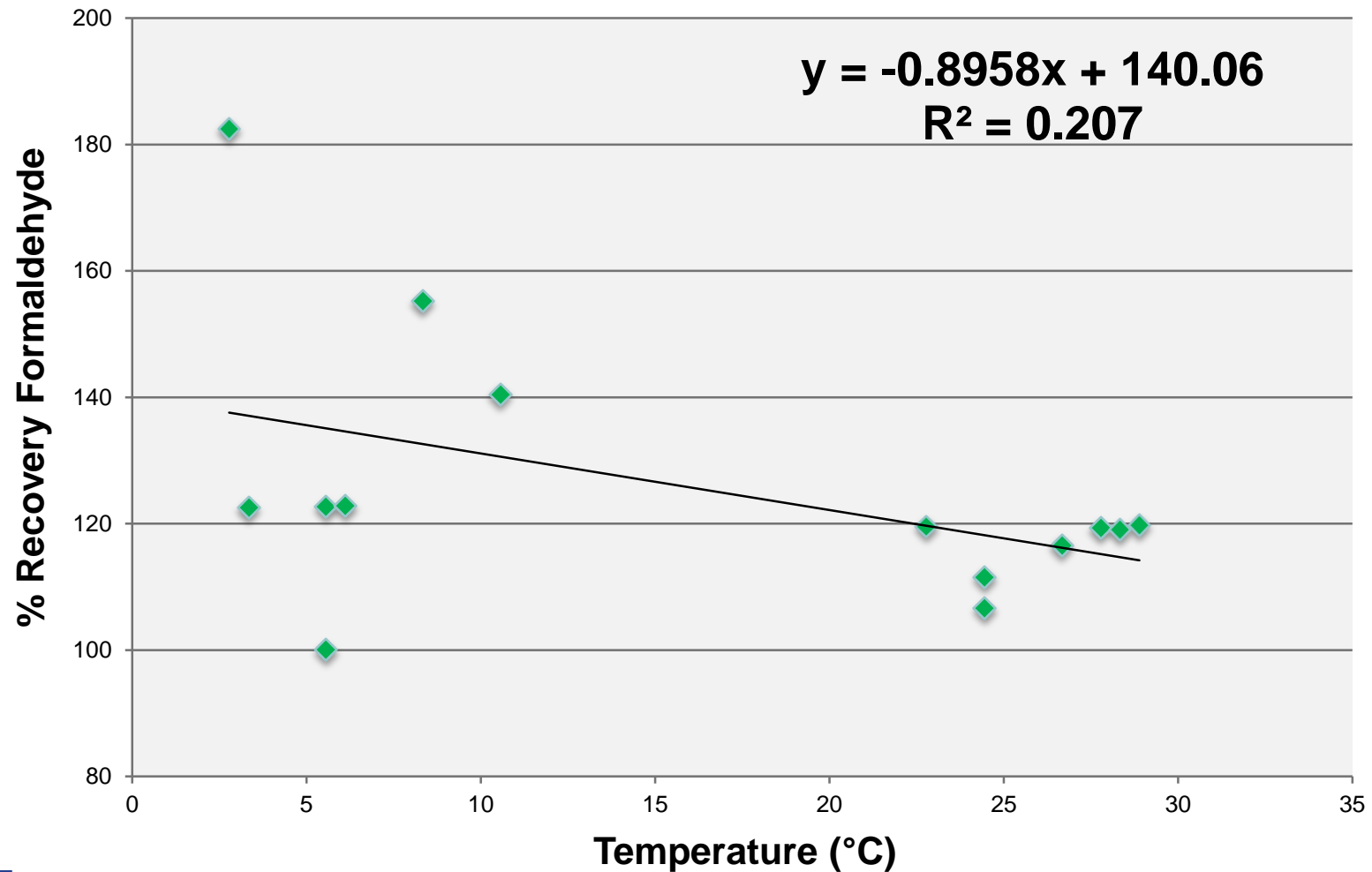
Relative Humidity Vs. Formaldehyde % Recovery





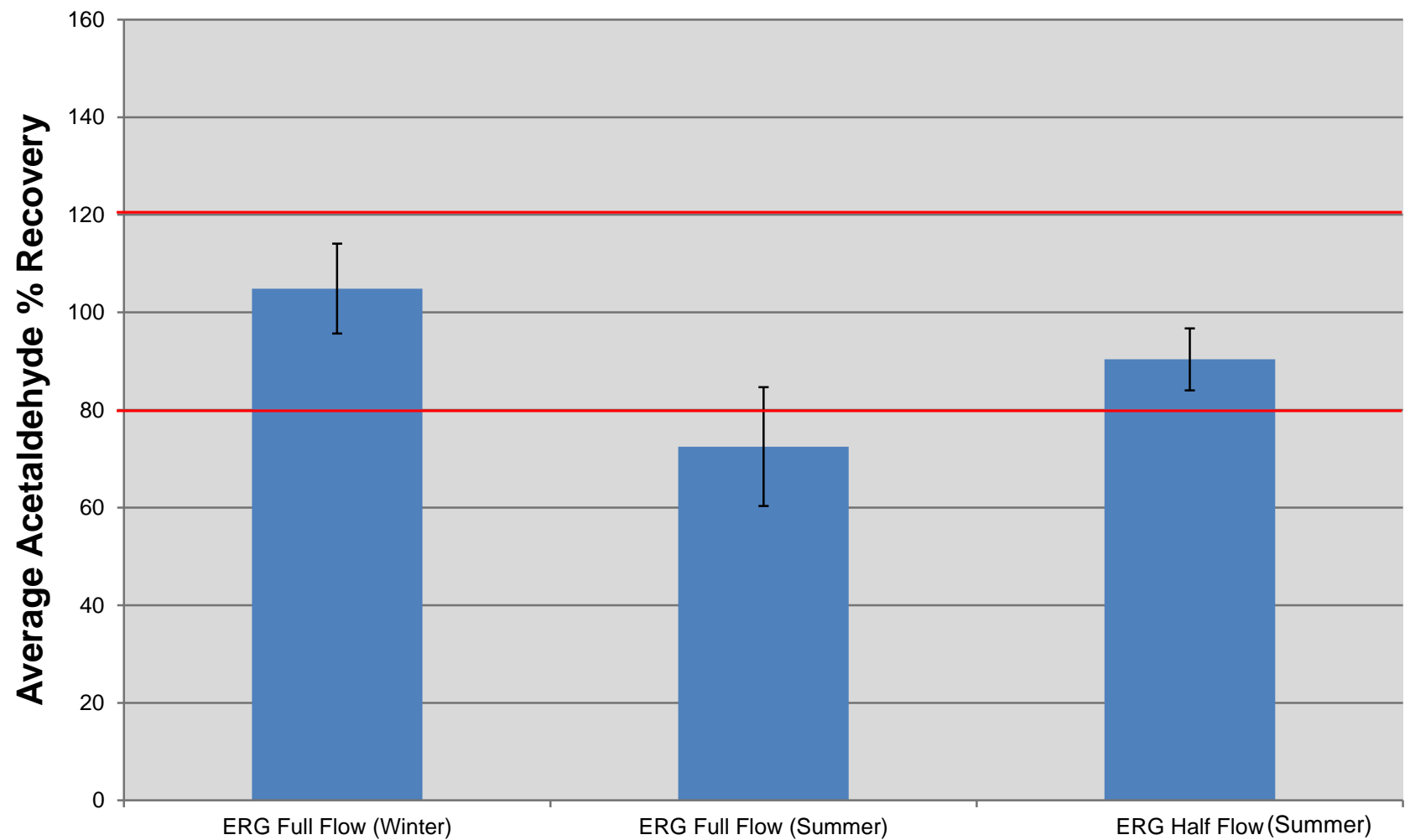
Study Results: Formaldehyde

Temperature Vs. Form % Recovery





Results: Acetaldehyde





Results: Acetaldehyde

Average % Recovery

ERG Full Flow (Winter) <i>7 samples</i>	104.86% (\pm 9.21%)
ERG Full Flow (Summer) <i>7 samples</i>	72.49% (\pm 12.18%)
ERG Half Flow (Summer) <i>3 samples</i>	90.37% (\pm 6.35%)



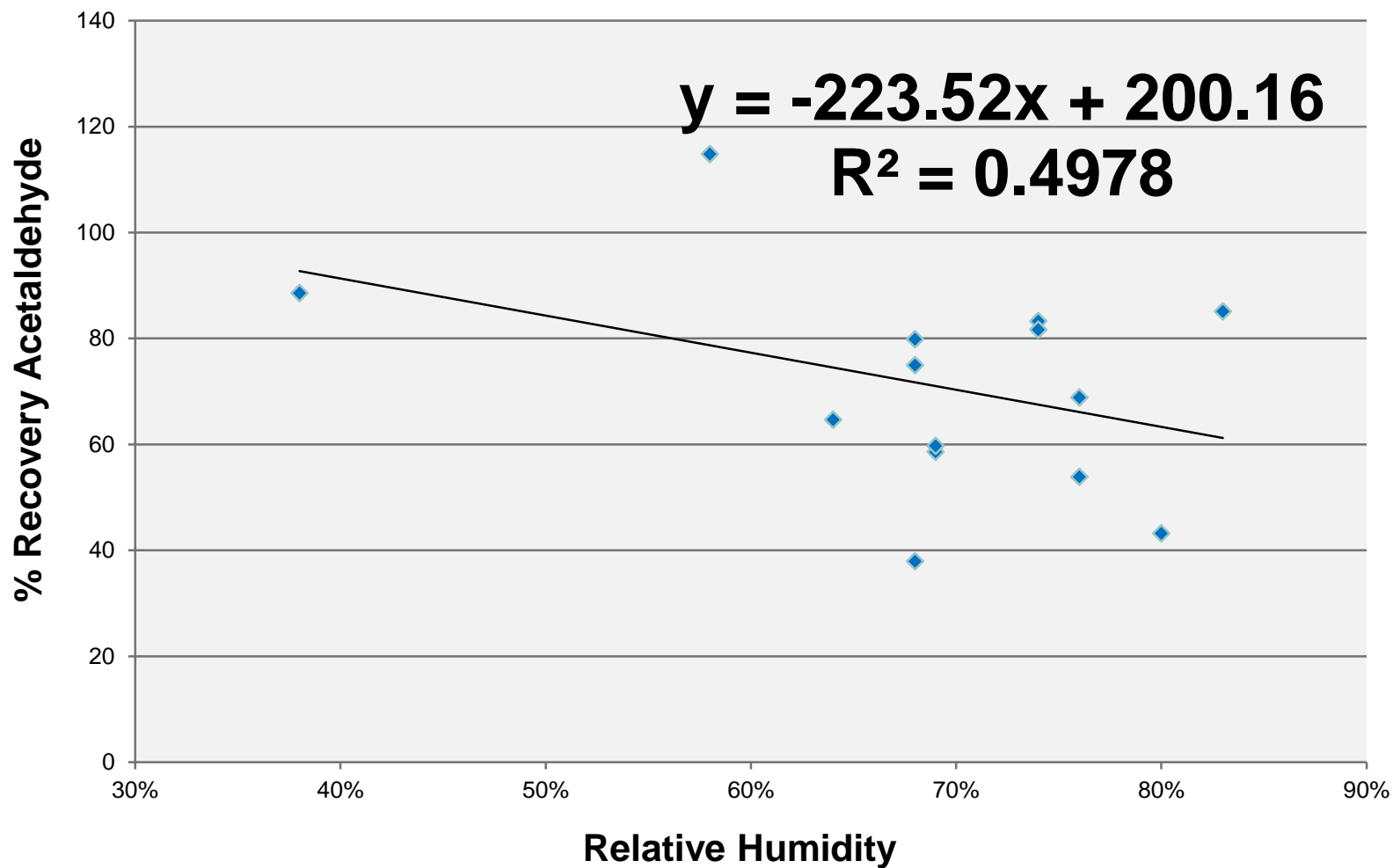
Results: Acetaldehyde

**Is the acetaldehyde recovery
affected by humidity?**



Results: Acetaldehyde

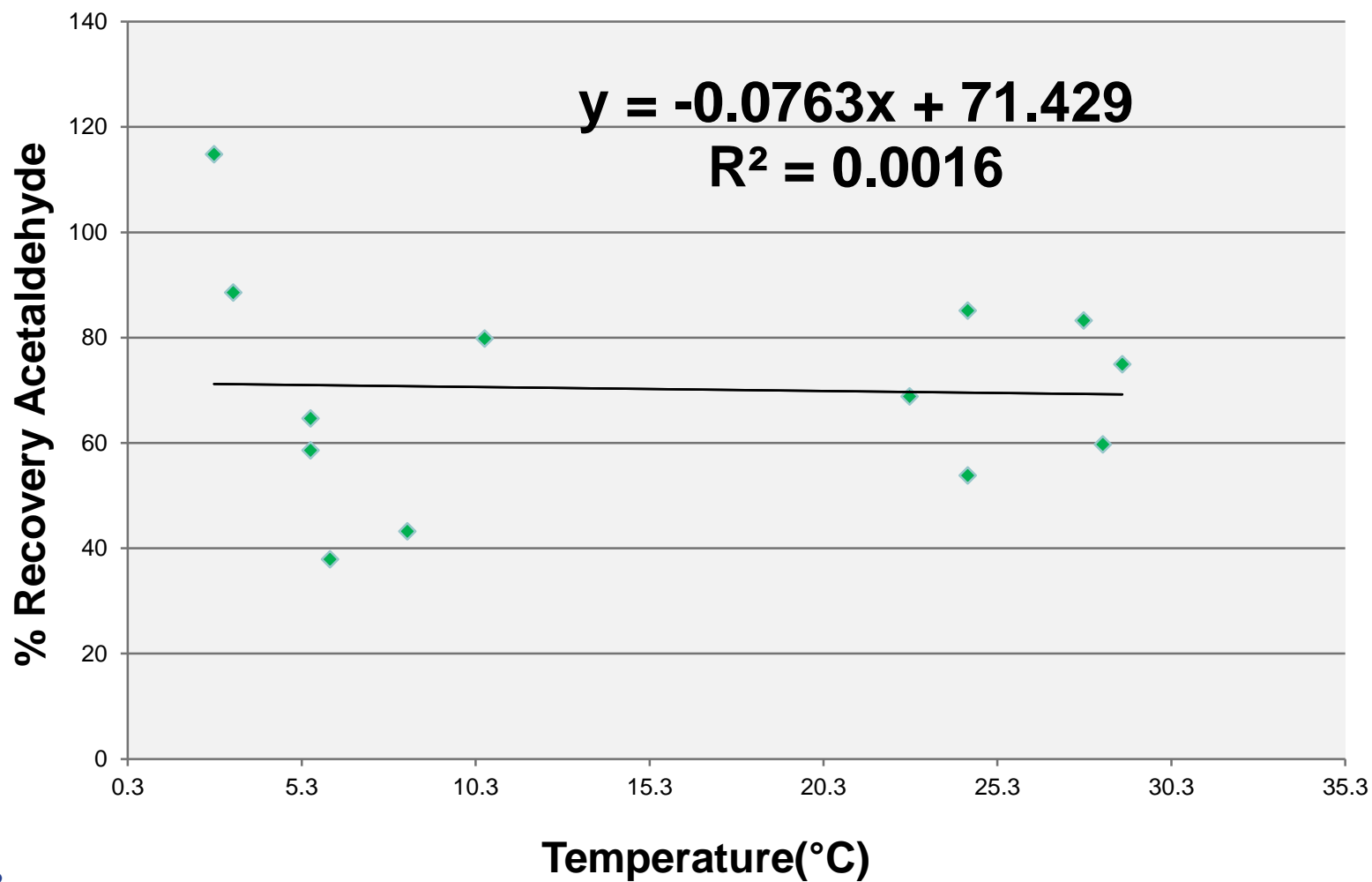
Relative Humidity Vs. Acetaldehyde % Recovery





Results: Acetaldehyde

Temperature Vs. Acetaldehyde % Recovery





Other Results

Full Flow, Winter **Full Flow, Summer** **Half Flow, Summer**

Compound	% Rec.	Passed?	% Rec.	Passed?	% Rec.	Passed?
Propionaldehyde	102.06	Y	81.23	Y	95.72	Y
Crotonaldehyde	90.94	Y	81.99	Y	87.67	Y
Butyraldehyde	97.25	Y	84.16	Y	92.95	Y
Benzaldehyde	88.55	Y	93.75	Y	96.65	Y
Isovaleraldehyde	104.94	Y	102.97	Y	100.85	Y
Valeraldehyde	107.24	Y	100.10	Y	100.24	Y
Tolualdehydes	96.98	Y	95.74	Y	96.73	Y
Hexaldehyde	98.20	Y	96.78	Y	98.01	Y
2,5-Dimethylbenzaldehyde	98.84	Y	102.85	Y	97.49	Y

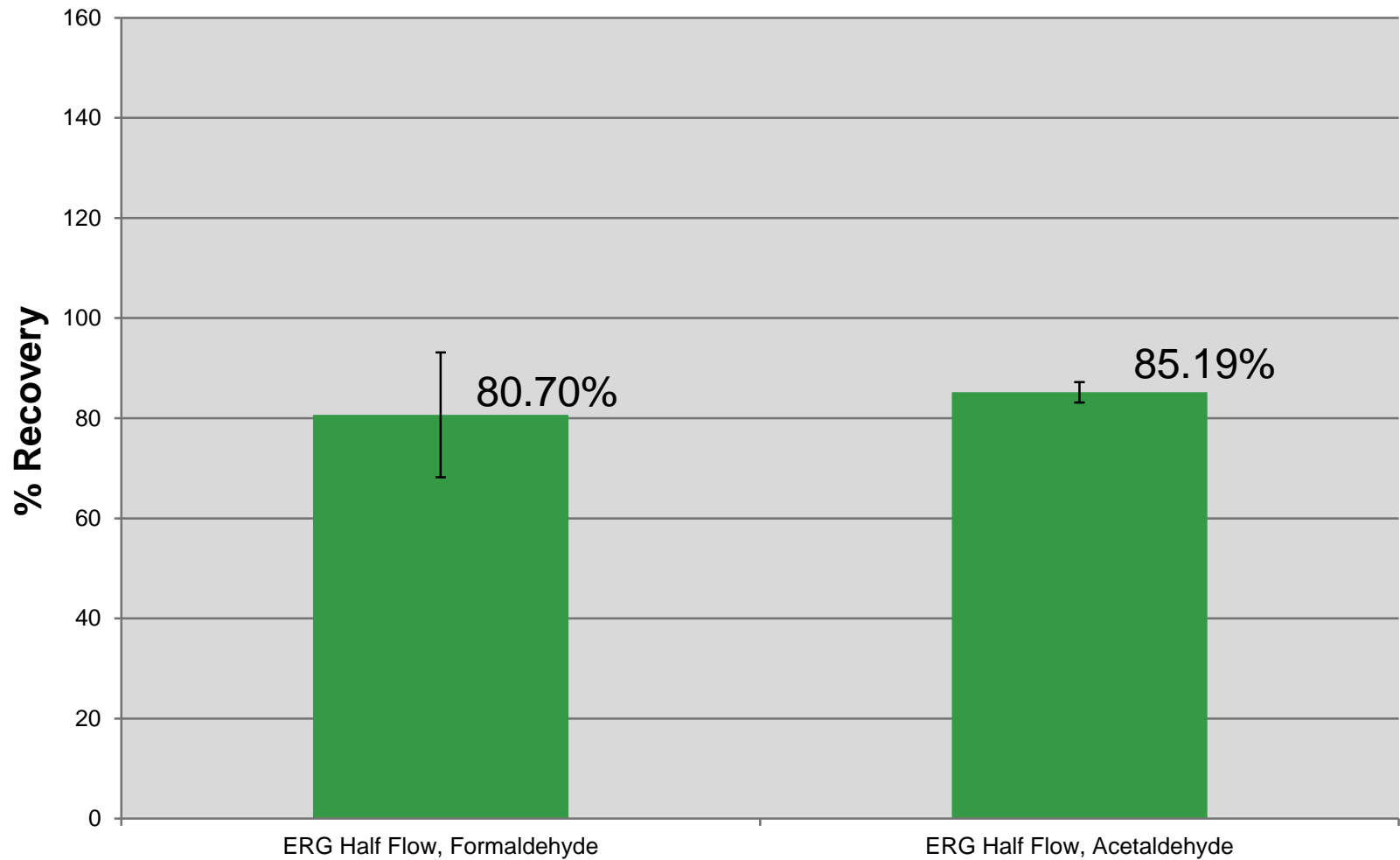


Further Studies: 2014

- Another round of spiked versus unspiked sampling occurred in 2014
- Three sites throughout the country participated in three rounds of sampling
- Most recoveries were too low



Further Studies: 2014

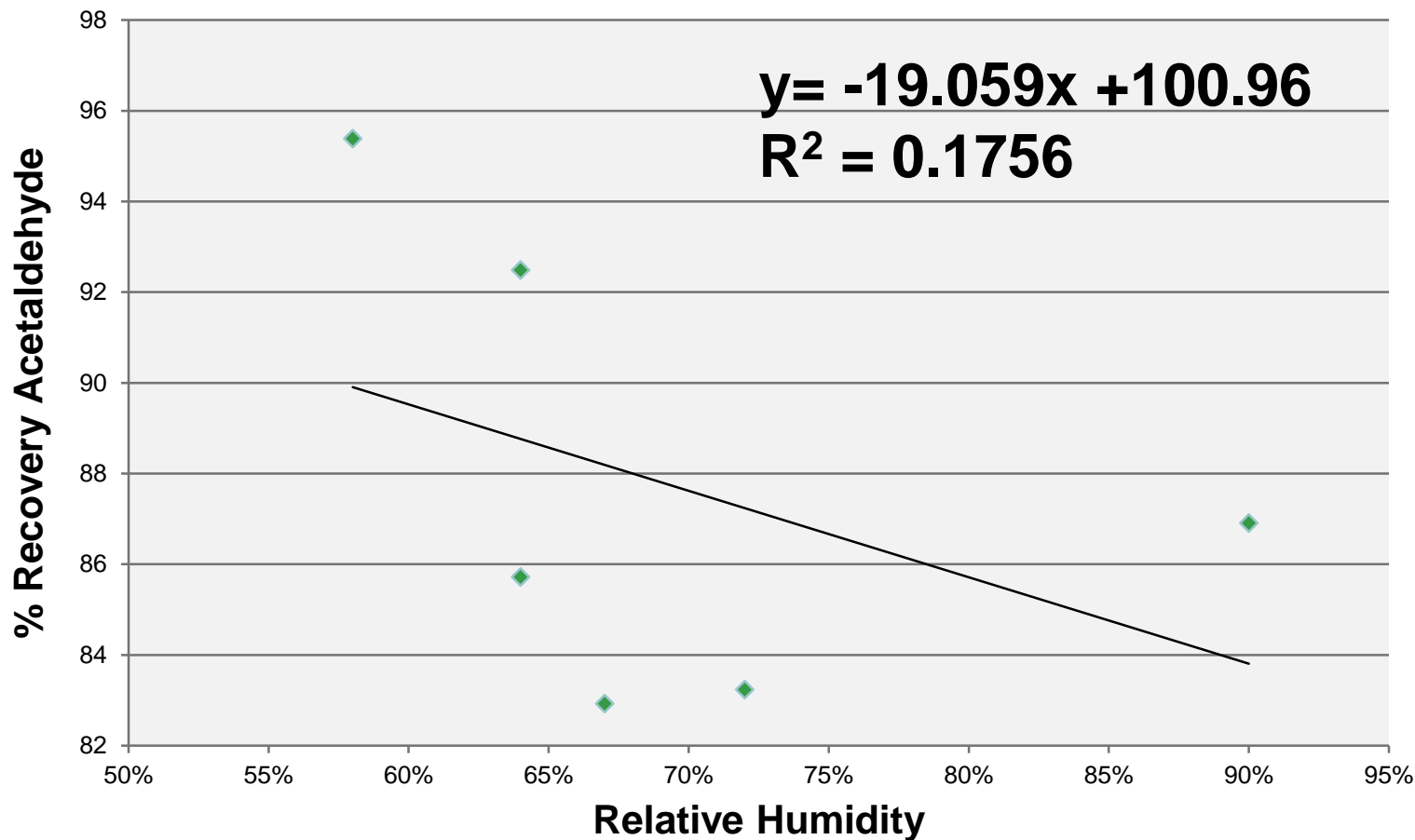


3 samples



Further Studies: 2014

Relative Humidity Vs. Acetaldehyde % Recovery





Summary

- Formaldehyde recoveries are acceptable
- Acetaldehyde recoveries are acceptable and do not seem to be affected by humidity
- The half-flow rate sampler is more effective for spike recovery than the full flow rate sampler
- Further studies are needed to ascertain the effectiveness of the TO-11A method



Future Work

- Perform stability studies to address potential issues with drop-off and pick-up times
- Breakthrough studies on half-flow sampler



Acknowledgements

- U.S. EPA
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Questions?